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Sampling and Analysis Considerations at Chemical Warfare Materiel Sites

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**DOD Environmental Monitoring & Data Quality
Workshop**

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Agenda



- **Terms**
- **Potential CWM Sites**
- **Contaminants of concern, to include chemical agents and agent breakdown products**
- **Analytical methods for chemical agents and ABPs**
- **DA PAM 385-61 environmental sampling requirements**
- **EP 75-1-3 environmental sampling requirements**
- **Laboratory requirements**
- **Chemical-specific criteria for environmental media**
- **Lessons Learned**



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Terms



- **Chemical Warfare Materiel (CWM):** An item configured as a munition containing a chemical substance that is intended to kill, seriously injure, or incapacitate a person through its physiological effects. Also includes V- and G- series nerve agents, H-series blister agent, and lewisite in other-than-munition configurations. Due to their hazards, prevalence, and military unique application, chemical agent identification sets (CAIS) are also considered CWM. **CWM does not include** riot control agents; chemical herbicides; smoke and flame producing items; or **soil, water, debris or other media contaminated with chemical agent**
- **Recovered Chemical Warfare Materiel (RCWM):** Non-stockpile CWM that was previously discarded, buried, or fired, and discovered either unexpectedly or during planned environmental restoration operations
- **Chemical Agent Contaminated Media (CACM)**



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Potential CWM Sites



- **Types of CWM Sites:**
 - RCWM
 - CACM (treated as HTRW site)
- **Evaluation is made based on site history**
- **Types of Sites that could contain RCWM or CACM include:**
 - Manufacturing Facilities
 - Storage Facilities (Depots, Terminals, Arsenals)
 - Military Training (Army Airfields, Camps, Forts, etc.)
 - Test Sites
- **Scoping & Security Study underway to evaluate FUDS sites with CWM Potential**



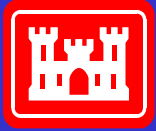
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CAIS Items Uncovered



K951 Vials
Raritan, New Jersey





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CAIS Items Uncovered



K951 PIGS
Mongmong, Guam



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Contaminants of Concern – CWM & Industrial Chemicals



- **Chemical Warfare Materiel**
 - Sulfur Mustard (HD, H, HS, HT)
 - Lewisite (L)
 - Nerve Agents [i.e., Tabun (GA), Sarin (GB), Soman (GD), VX]
 - Nitrogen Mustard (HN1, HN3)
- **Industrial Chemicals**
 - Other CAIS Constituents [Adamsite (DM), Phosgene (CG), Chloroacetophenone (CN), Chloropicrin (PS), Cyanogen Chloride (CK), Chloroform]*

* These constituents not typically analyzed in soil due to lack of method, lack of persistence, or lack of specificity to CWM sites

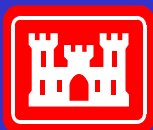


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Contaminants of Concern – Breakdown Products



- **Sulfur Mustard**
 - 1,4-Dithiane
 - 1,4-Oxathiane
 - Thiodiglycol (TDG)
- **Lewisite**
 - 2-Chlorovinyl Arsenous Acid (CVAA)
 - 2-Chlorovinyl Arsenous Oxide (CVAO)
- **Nitrogen Mustard**
 - Triethanolamine (TEA)
 - Diethanolamine (DEA)
 - Ethyl Diethanolamine
- **Nerve Agents**
 - Isopropyl Methylphosphonic Acid (IMPA)
 - Methylphosphonic Acid (MPA)
 - Dimethyl methylphosphonate (DMMP)
 - Ethyl Methylphosphonic Acid (EMPA)
 - Diisopropyl Methylphosphonate (DIMP)



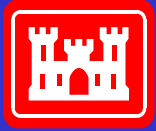
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Analytical Methodology

- GC/MS - H, L (with CVAA and CVAO)*, GA, GB, GD, VX, HN1, HN3, 1,4-Dithiane, 1,4-Oxathiane, and TDG
- GC – DMMP and DIMP
- HPLC - TDG
- IC – IMPA, MPA, and EMPA
- Capillary Electrophoresis – DEA, TEA, and Ethyl Diethanolamine

* L, CVAA, and CVAO must be derivatized and form the same derivative. They are analyzed and reported together.

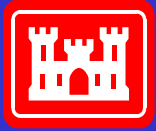


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DA PAM 385-61 Requirements



- **Current Version - 27 March 2002**
- **Addresses Shipment of Environmental Samples (10-6)**
- **“Environmental samples may consist of soils and other solids, water, sludge, and vegetation. Prior to packaging, samples will be screened using either airborne (ensure concentrations are below the AEL), or soil extraction methods (ensure agent concentrations are below detectable levels).**
- **Packaging is as follows:**
 - a. Solids, water, and sludge are usually packed in glass jars with a screw top. The top of each jar is sealed with parafilm.
 - b. Vegetation samples may be contained in securely sealed plastic bags.
 - c. Such samples are packed in coolers with cold packs. The coolers are overpacked in wooden boxes to provide a stronger packaging.”



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EP 75-1-3



- **Current Version 4 January 2002, In Revision**
- **Written for Recovered Chemical Warfare Materiel (RCWM) Response; however, similar precautions are appropriate for Chemical Agent Contaminated Media (CACM) projects. No comparable guidance exists for CACM projects.**
- **Purpose of Environmental Sampling:**
 - To determine if residual chemical agent contamination from a release, spill or disposal operation is present in the surrounding environment and/or
 - To determine if other industrial chemicals are mixed with the chemical agent of concern.



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EP 75-1-3 Requirements



- **Addresses Environmental Sampling (9.5)**
- **Media:**
 - Soils and other solids, Water, Sludge, and Vegetation
- **Sample Locations:**
 - Immediately beneath and/or adjacent to any RCWM
 - Surrounding media whenever there are visual or airborne indicators of potential chemical agent contamination.
 - Based on Historical Information
- **Sample Clearance:**
 - Prior to off-site shipment, all samples will be screened for agent using either airborne methods to ensure concentrations are below the AEL or soil and water extraction methods to ensure concentrations are below detectable levels IAW DA Pam 385-61.

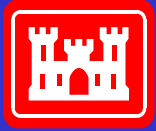


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EP 75-1-3 Requirements for HTRW Samples



- **Per EP 75-1-3, If Sub-samples of Environmental Samples are to be Analyzed for HTRW Contaminants, the Following Procedures will be Followed:**
 - Samples will be Homogenized prior to Division
 - Sub-samples will be Retained on-site or at a Chemical Surety Laboratory until Split Samples have been Analyzed by Extraction and Determined to have no detectable levels of Chemical Agent Contamination
 - Sub-samples will be Head-spaced Prior to Off-site Shipment to Ensure Concentrations are Below the AEL
 - The Receiving Laboratory to conduct HTRW analysis is notified in Writing that Samples could Possibly Contain Chemical Agent Contamination.



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Agent Laboratory Requirements



- **Government laboratory approved to handle dilute agents or commercial laboratory with current bailment agreement (“surety laboratories”)**
- **Conformance with Chemical Agent Standards Analytical Reference Material (CASARM) Plan**
- **Laboratory QA/QC Plan and SOPs for applicable agent analyses**



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Criteria for Environmental Media

				H/HD/HT	GA	GB	GD/GF	VX	Lewisite
SOIL (mg/kg)	HBESL- Residential	adults and children	daily exposure, lifetime	0.01	2.8	1.3	0.22	0.042	0.3
	HBESL- Industrial	adults	frequent exposures 250 days/yr. For 30 years	0.3	68	32	5.2	1.1	3.7

Sources:

- *Health-Based Environmental Screening Levels for Chemical Warfare Agents*, USACHPPM/ORNL Technical Report, March 99.
- Memorandum, Headquarters Department of the Army, Office of the Assistant Secretary for Installations, Logistics, and Environment, SUBJ: Derivation of Health-Based Environmental Screening Levels (HBESLs) for Chemical Warfare Agents, May 28 1999.

Uses EPA Region IX PRG soil risk assessment methods



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Lessons Learned



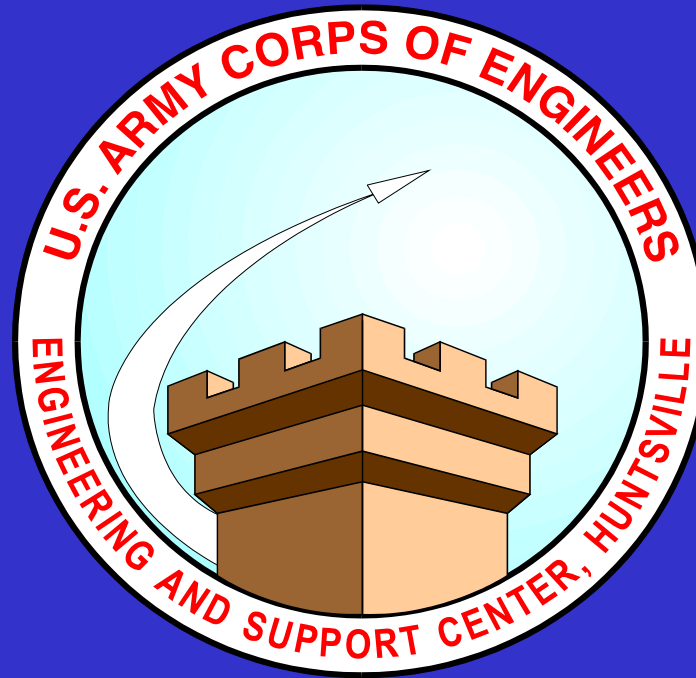
- **Use On-site RCWM Lab or Maintain Close Coordination with Agent Lab to Meet Holding Times for HTRW Samples**
- **Freeze VOC samples**
- **Logistics are Problematic for Maintaining Temperature of On-site Samples**
- **Agent Lab and Contractor must ensure Appropriate Analyses are Requested and Performed as work is Executed**



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ANY QUESTIONS?



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